



Influence of a cyclic butylene terephthalate oligomer on the processability and thermoelectric properties of polycarbonate/MWCNT nanocomposites



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ABSTRACT

The thermoelectric properties of melt-processed nanocomposites consisting of a polycarbonate (PC) thermoplastic matrix filled with commercially available carboxyl (–COOH) functionalized multi-walled carbon nanotubes (MWCNTs) were evaluated. MWCNTs carrying carboxylic acid moieties (MWCNT-COOH) were used due to the p-doping that the carboxyl groups facilitate, via electron withdrawing from the electron-rich π -conjugated system. Preliminary thermogravimetric analysis (TGA) of MWCNT-COOH revealed that the melt-mixing was limited at low temperatures due to thermal decomposition of the MWCNT functional groups. Therefore, PC was mixed with 2.5 wt% MWCNT-COOH (PC/MWCNT-COOH) at 240 °C and 270 °C. In order to reduce the polymer melt viscosity, a cyclic butylene terephthalate (CBT) oligomer was utilized as an additive, improving additionally the electrical conductivity of the nanocomposites. The melt rheological characterization of neat PC and PC/CBT blends demonstrated a significant decrease of the complex viscosity by the addition of CBT (10 wt%). Optical and transmission electron microscopy (OM, TEM) depicted an improved MWCNT dispersion in the PC/CBT polymer blend. The electrical conductivity was remarkably higher for the PC/MWCNT-COOH/CBT composites compared to the PC/MWCNT-COOH ones. Namely, the PC/MWCNT-COOH/CBT processed at 270 °C exhibited the best values with electrical conductivity; $\sigma = 0.05$ S/m, Seebeck coefficient; $S = 13.55$ μ V/K, power factor; $PF = 7.60 \times 10^{-6}$ μ W/m K², and thermoelectric figure of merit; $ZT = 7.94 \times 10^{-9}$. The PC/MWCNT-COOH/CBT nanocomposites could be ideal candidates for large-scale thermal energy harvesting, even though the presently obtained ZT values are still too low for commercial applications.

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1. Introduction

The incorporation of carbon nanotubes (CNTs) in polymer matrices has been the subject of various studies, demonstrating that they are an ideal candidate for fabricating multifunctional polymer nanocomposites [1–6].

Recently, polymers filled with CNTs have been proposed as thermoelectric (TE) power generators, and an extensive scientific interest has been rapidly grown [7,8] [9]. Thermoelectric materials (TE) are one potentially alternative source of energy, due to their ability to generate voltage upon exposure to a temperature

gradient. Nowadays, there is a huge concern regarding the finite supply of fossil fuels. Therefore, energy harvesting from environments where huge amounts of waste thermal energy are generated is of outmost importance. The performance of thermoelectric materials is characterized by a dimensionless figure of merit (ZT); $ZT = (\sigma \times S^2 / \kappa) T$, where σ represents the electric conductivity (S/m), S the Seebeck coefficient (μ V/K) defined as $S = \Delta V / \Delta T$ (ΔV : the electric potential difference or thermoelectric voltage created by the temperature gradient ΔT), κ the thermal conductivity (W/mK), and T the absolute temperature (K) [10]. The quantity $\sigma \times S^2$ is known as the power factor (PF), and it is also used as a means to compare the thermoelectric efficiency of different materials. The Seebeck coefficient can be positive for p-type semi-conductors or negative for n-type ones, while it is an intrinsic property of the

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materials related to their electronic properties and independent of their geometry [11,12]. Moreover, it is easily realized that for an optimum thermoelectric efficiency, a high electrical conductivity combined with high Seebeck coefficient and low thermal conductivity are required. Traditional thermoelectric materials are generally represented by narrow band gap semiconductors; i.e. Bi_2Te_3 , PbTe , etc., however they are limited in use due to toxicity and viability in the up-scaling of their production [13,14]. CNT-based polymer nanocomposites are of particular interest due to their low thermal conductivity, high electrical conductivity, versatile production, relatively low cost, environmentally benign characteristics, flexibility and high specific properties [15]. The CNT networks in a polymer matrix allow the electron transport by a tunneling or a hopping mechanism when junctions are separated by an insulating polymer film (even if 1.8 nm thickness) [16]. At the same time, phonon scattering at the CNT-polymer-CNT interphases will prevent their effective transmission through the composite, resulting in low thermal conductivity values. The low thermal conductivity allows the temperature difference to be sustained within the material inducing thus the generation of charge carriers. Hence, polymer/CNT nanocomposites fulfill quite well the demands for an efficient thermoelectric material taking into account the previous formula of the thermoelectric figure of merit.

Investigations of carbon nanotubes' thermoelectric efficiency have shown promising results, found to be related to the level of doping [17,18] as well as the nature of the dopant molecule [19–23]. Hewitt et al. showed that the Seebeck coefficient of MWCNT buckypapers was in the range of 11–19 $\mu\text{V/K}$, and proved that only the treatment with oxygen containing acids, such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3), caused an increase in the Seebeck coefficient of MWCNTs [17]. Recently, it has been also reported that SWCNTs can exhibit an improved thermoelectric behavior depending on the nature of the dopant [24]. Moreover, in another study it was shown that doping of SWCNTs using e.g. polyethyleneimine (PEI) or hexafluoroacetone [25,26] resulted in Seebeck coefficients up to $-50 \mu\text{V/K}$.

Until now, several studies exist in which polymer/CNT nanocomposites have been examined for their thermoelectric performance [14,27–31]. In most of the cases, composites fabricated by solution mixing techniques were tested; however, it is known that this is not a viable method for up-scaling the production process. Relatively high filler loadings ($>50 \text{ wt}\%$) can be realized [31], which result further in quite high electrical conductivities [32–36]. More specific, polymer composites with electrical conductivities up to $4 \times 10^5 \text{ S/m}$, and power factors in the range of $\sim 140 \mu\text{W/mK}^2$ have been reported for single-walled carbon nanotubes (SWCNTs) in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) matrix [37]. In general, CNT-polymer composites based on an electrically conductive matrix such as polyaniline (PANI) [34,36–38], polythiophene (PT), and PEDOT have been reported several times [32,37], however, these polymers do not fulfill the requirements for thermal stability at high temperatures as compared to engineering polymers. Furthermore, Seebeck coefficients between 10 and 30 $\mu\text{V/K}$ were reported for polythiophene/MWCNT and PANI/graphite composites [28,38].

For composites of SWCNTs and PC prepared by solvent mixing, it was shown that by increasing the SWCNT content (up to 30% wt%), the electrical conductivity increased to approximately 1000 S/m and the Seebeck coefficient reached the value of 60 $\mu\text{V/K}$ being slightly dependent on the SWCNT content [25]. Furthermore, Seebeck coefficients up to 10 $\mu\text{V/K}$ were reported for expanded graphite in PC, which could be slightly improved up to 12 $\mu\text{V/K}$ by using additional polymers (PEDOT and PSS) [39]. SWCNT composites with polymers having electron rich functional groups, like PVA and PEI, resulted due to n-doping in coefficients up to $-21.5 \mu\text{V/K}$ [26].

The only study which addresses the thermoelectric properties of melt-mixed polymer/CNT composites can be found in the work of Antar et al. [40]. Polylactide (PLA)/MWCNT and PLA/expanded graphite composites were prepared, and high loadings up to 30 wt% were achieved resulting in electrical conductivities of around 4000 S/m. Maximum Seebeck coefficients of 17 $\mu\text{V/K}$ for composites with expanded graphite and about 9 $\mu\text{V/K}$ with MWCNTs were found, however, a strong increase of the thermal conductivity to about 5.5 W/m K^{-1} was observed.

In the present work, a facile melt-mixing process was utilized to fabricate polycarbonate/MWCNT nanocomposites, and the thermoelectric properties have been investigated in detail. The literature survey has shown that doping of CNTs has a positive impact on the Seebeck coefficient values [24–26]. Therefore, commercially available carboxyl functionalized MWCNTs (MWCNT-COOH) have been used to incorporate them in an engineered thermoplastic polycarbonate matrix. It has been already found that for polycarbonate composites prepared at 300 °C, this particular MWCNT functionalization results in higher Seebeck coefficients compared to unfunctionalized MWCNTs [9]. However, the thermogravimetric analysis (TGA) of the MWCNT-COOH showed that the melt-mixing process is limited to relatively low temperatures in order to avoid possible decomposition of the MWCNT functional groups. To be able to perform melt mixing to lower temperatures, a cyclic butylene terephthalate (CBT[®]) oligomer was used as a low molecular additive to reduce the polymer melt viscosity. This particular oligomer has been investigated in several polymer/CNT systems in order to obtain enhanced electrical conductivity as well as mechanical reinforcement [41–47]. PC/MWCNT-COOH conductive composites with a constant amount of MWCNT-COOH (2.5 wt%) were prepared at 240 and 270 °C, with or without the CBT oligomer. These are relatively low processing temperatures for the used PC, which typically range between 280 °C and 320 °C. The morphology of the final nanocomposites was investigated and compared by optical and transmission electron microscopy (OM, TEM). Finally, the electrical conductivity, thermal conductivity, and thermoelectric properties were examined and correlated to the nanocomposite's morphological characteristics.

2. Experimental section

2.1. Materials

The polycarbonate type Makrolon[®] PC 2205 (Bayer MaterialScience, Leverkusen, Germany) with a density of 1.2 kg/m^3 and a glass transition temperature (T_g) of $\sim 145 \text{ °C}$ was used in this study. The cyclic butylene terephthalate oligomer (CBT[®] 100) employed as an additive for decreasing the melt viscosity of PC was obtained from Cyclics Corporation, USA. The number of repeating unit in the cyclic oligomer varies from two to seven according to the supplier's specification; the material is free of catalyst. The chemical structures of PC and CBT are shown in Fig. 1. The addition of CBT (10 wt%) to PC resulted in a decrease of T_g to 126 °C.

Commercially available MWCNTs containing carboxylic acid groups (MWCNT-COOH, $\geq 95\%$ purity), with the trade name Nanocyl[®] NC3151, were purchased from Nanocyl S.A. (Sambreville, Belgium), and they have an oxygen content of around 6.3 at% [9].

2.2. Sample preparation

The PC/CBT, PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites were prepared in a one-step melt-mixing process using a DSM Xplore Microcompounder (Geleen, Netherlands) having

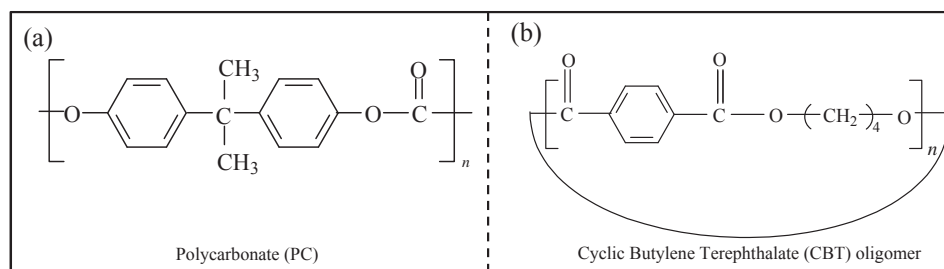


Fig. 1. Chemical structure of (a) polycarbonate, and (b) CBT oligomer (n represents the number of repeating units ranging between 2 and 7).

a capacity of 15 cm^3 . This microcompounder consists of two conical co-rotating screws with a bypass, allowing the material to circulate within the machine for defined periods. The mixing process was performed using the following parameters: 150 rpm as a constant rotational speed of the screws, 5 min as the mixing time, and mixing temperatures of 240°C and 270°C . The unfilled PC/CBT blend consisted of 90 wt% PC and 10 wt% CBT, the PC/CBT/MWCNT-COOH composite was composed of 87.5 wt% PC, 10 wt% CBT and 2.5 wt% MWCNT-COOH, while the PC/MWCNT-COOH composite without additive contained 97.5 wt% PC and 2.5 wt% MWCNT-COOH. By that, the amount of MWCNT-COOH was kept constant at 2.5 wt%. Prior to the compounding process, the materials were vacuum dried at 80°C overnight and premixed in a glass vial. The materials were then fed via a hopper into the microcompounder at the aforementioned processing speed. After the completion of the mixing process, the material was taken out from the compounder as an extruded strand without additional cooling. The neat PC was treated in the same manner.

Compression molding was used in order to prepare the specimens for all the characterization techniques in this study. For the electrical conductivity and thermovoltage measurements, the extruded strands were cut into short pieces and pressed under vacuum into circular plates of 25 mm diameter and 0.8 mm thickness using the Weber press (PW 20, Paul Otto Weber; Remshalden, Germany). The compression molding temperature was equal to the melt mixing temperature, while the pressure was set for all samples at 17.5 kN. Subsequently, the temperature control was stopped, and the cooling process started.

The rheological properties and thermal conductivity of all samples were determined on specimens prepared using the Weber press (PW 40, Paul Otto Weber; Remshalden, Germany). For rheology, plates with 1.5 mm thickness and 25 mm diameter were molded at mixing temperature for 2 min with 50 kN. For the thermal conductivity measurements, plates having a diameter of 12.5 mm and a thickness of 2 mm were prepared following the

same procedure. Afterwards, the samples were cooled inside a minichiller.

2.3. Characterization

2.3.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a TA instrument (Q 5000). The temperature range varied from ambient (25°C) up to 800°C , with 10 K/min heating rate, under a oxygen atmosphere. Curie point standards were utilized for the temperature calibration.

2.3.2. Rheological measurements

The melt rheological investigations were performed with an ARES oscillatory rheometer (Rheometric Scientific Inc., USA) under liquid nitrogen. A plate–plate geometry with 1.5 mm gap was used. Before reaching the measurement position, the samples were melted at the corresponding processing temperatures of 240°C or 270°C . Frequency sweeps from 0.063 rad/s to 100 rad/s and back were accomplished at the corresponding temperature with an applied strain of 10%. The results presented in this work have been obtained from measurements ranging from 100 rad/s down to 0.063 rad/s.

2.3.3. Morphological analysis of the composites

The morphological characterization was carried out on the extruded strands perpendicular to the melt flow direction. The quantification of the MWCNT macro-dispersion in the polymer matrix was performed by light optical microscopy (OM). Thin sections of $\sim 5 \mu\text{m}$ thickness were cut from the extruded strand at room temperature using a Leica RM2265 microtome (Leica Microsystems GmbH, Wetzlar, Germany), and fixed on a glass plate. An Olympus BH2 microscope in transmission mode, combined with a DP71 CCD camera (Olympus Germany GmbH; Hamburg, Germany) was used for the section imaging. The state of dispersion was determined by

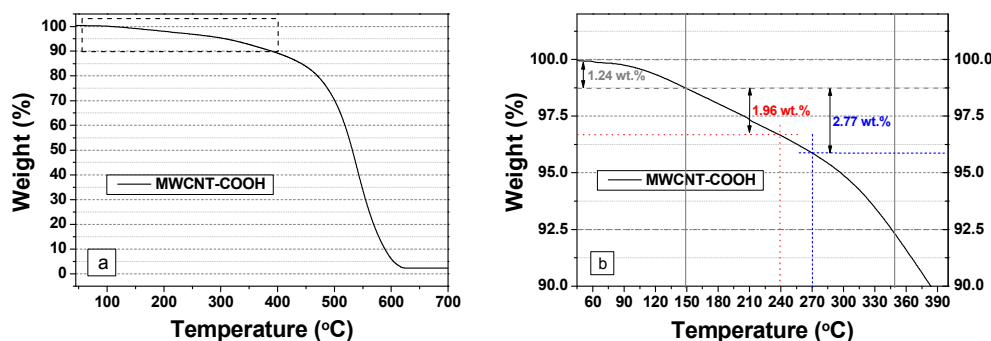


Fig. 2. TGA curves of MWCNT-COOH in the temperature region of (a) 45 – 700°C , and (b) 45 – 400°C showing more precisely the weight loss up to 240 and 270°C , the temperatures selected for the melt-mixing process (reproduced from Ref. [9], Supplementary material).

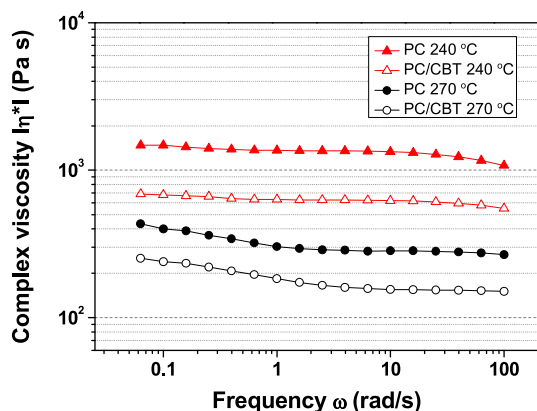


Fig. 3. Complex viscosity η^*I of the PC and PC/CBT blends prepared and measured at different temperatures, versus oscillation frequency ω .

analyzing the remaining, black appearing MWCNT agglomerates in the recorded image. These were quantified by calculating the agglomerate area ratio (A_A) using the ImageJ 1.47n software. At least 10 individual recorded images at the same magnification were used for the calculations. To exclude impurities that were introduced during sample preparation or observation, particles with a circle equivalent diameter lower than 5 μm were excluded from the calculation of the A_A .

Transmission electron microscopy (TEM) images were recorded in order to evaluate the MWCNT nano-dispersion in the polymer matrix. Ultrathin sections of approximately 50–70 nm thickness were prepared by ultramicrotomy using a Leica ultramicrotome (Leica UC7, Leica Microsystems GmbH, Wetzlar, Germany) at room temperature. Diamond knives for cryo-temperatures (Diatome) were used for the trimming (model cryotrim 45°) as well as the cutting process (model cryo 35°). The TEM images were acquired

using the Libra200 (Carl Zeiss AG, Oberkochen, Germany) transmission electron microscope operating at an acceleration voltage of 200 kV. Bright field TEM images were recorded while the energy filtering and contrast apertures were inserted in order to enhance the contrast of the images.

2.3.4. Electrical and thermal conductivity measurements

Determination of bulk electrical conductivity of the composites was performed by measuring the volume resistivity of each specimen using strips cut from the compression molded plates. Samples with a resistance above 10^3 Ohm were measured with a Keithley 6517A electrometer (Keithley Instruments Inc., Cleveland, USA), whereas for the samples with a resistance below 10^3 Ohm, a Keithley multimeter DMM 2000 was used. Both resistance measurements were combined with a 4-point measurement cell (external source electrodes spacing 16 mm and measuring electrodes spacing 10 mm). The values reported are mean values of at least four measurements on different samples.

The thermal conductivity measurements were performed using the Netzsch LFA 447 Nano Flash (Netzsch equipment manufacturing GmbH, Selb, Germany), based on the laser flash principle. Both electrical and thermal conductivity measurements were carried out at room temperature.

2.3.5. Thermoelectric-power measurements

For the determination of the Seebeck coefficient, a self-made custom set-up designed at the Leibniz Institute of Polymer Research Dresden was used [9]. Composite strips of 2–3 mm width, 20–25 mm length and 0.8 mm thickness were mounted on two metal blocks, which allows the generation of a temperature gradient. For all measurements, one block was kept at room temperature (~ 298 K), while the other one was heated in a controlled manner with 10 K steps up to 373 K within a time frame of 40 min. The distance between the two blocks was set to 15 mm. The generated thermovoltage (ΔV) was measured across the electrodes

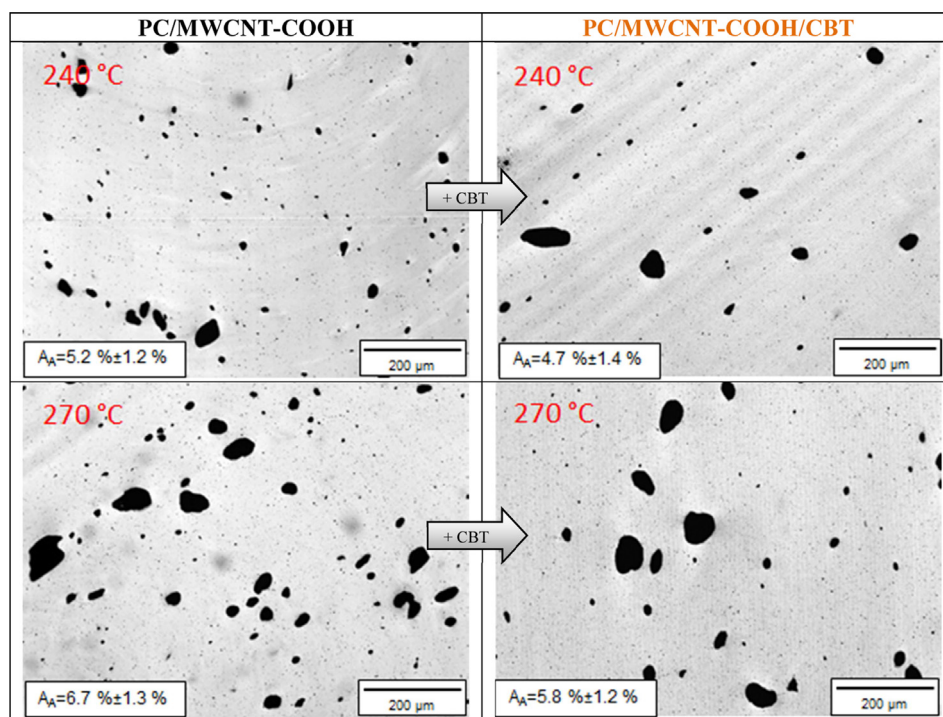


Fig. 4. Optical micrographs of the PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites with 2.5 wt% filler, showing different states of MWCNT macrodispersion due to the influence of the CBT additive. A_A represents the agglomerate area ratio of each sample.

by a Keithley 6517A (Keithley Instruments Inc., Cleveland, USA) interfaced with a computer. The temperature of the two blocks was continuously measured with K-type thermocouples to determine the temperature gradient, ΔT . The Seebeck coefficient was derived from the slope of ΔV vs ΔT curves by linear fitting, and the power factors as well as the thermoelectric figure of merits have been calculated.

3. Results and discussion

3.1. TGA of MWCNT-COOH

Thermogravimetric analysis (TGA) is a useful method to characterize carbon nanotubes with respect to the different structural forms as well as the existence of reactive side-wall functional groups [48]. It is known that for carboxylated MWCNTs, the weight loss up to 150 °C corresponds to the adsorbed moisture, which may be difficult to remove even after extensive drying [5]. From 150 °C to 350 °C, the weight loss is attributed to the decomposition of carboxylic acid groups attached to the MWCNTs [48]. Fig. 2a depicts the TGA curve of MWCNT-COOH in the temperature range of 45–700 °C. The area marked with the dashed rectangle is shown in Fig. 2b, representing the region between 45 and 400 °C. Fig. 2b shows more precisely the weight loss up to 240 °C and 270 °C, temperatures used for the composite fabrication. As it can be

observed, up to 240 °C there is a weight loss of 1.96 wt%, while up to 270 °C about 2.77 wt% weight loss occurs. Therefore, 270 °C was the highest temperature selected for the melt-mixing process, since further increase of the temperature can have a detrimental effect on the functional groups of MWCNTs. The MWCNT-COOH contained 11.67 wt% of –COOH according to our previous study [9].

3.2. Rheological characterization of neat PC and PC/CBT blends

Fig. 3 demonstrates the complex viscosities of neat PC and PC/CBT blends. As it can be observed, at 240 °C processing and measuring temperature the PC melt exhibits relatively high values of complex viscosity exceeding 1000 Pa s. The addition of CBT can remarkably decrease the complex viscosity values, reaching around the half of the initial ones. The same trend was also found for the PC/CBT blend processed at 270 °C. It should be mentioned that a slight effect of shear thinning was observed at higher frequencies for all the investigated samples being most prominent for pure PC.

3.3. Composite microstructure investigations

Fig. 4 shows the optical micrographs of the PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites processed at 240 °C and 270 °C. As shown in our study before, the dispersion of COOH modified nanotubes is much more difficult and results in worse

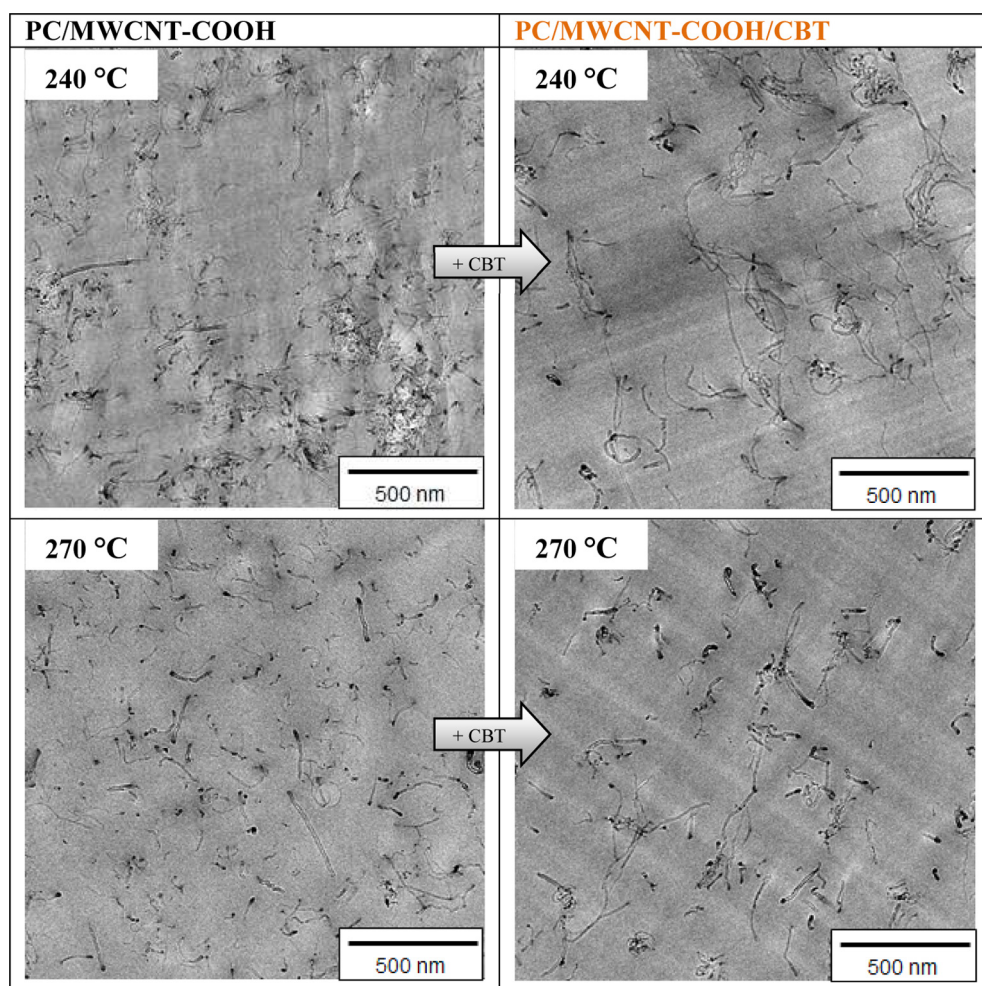


Fig. 5. TEM images of the PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites with 2.5 wt% MWCNT mixed at 240 °C and 270 °C. The TEM images depict the different states of MWCNT nanodispersion with or without the addition of the CBT oligomer.

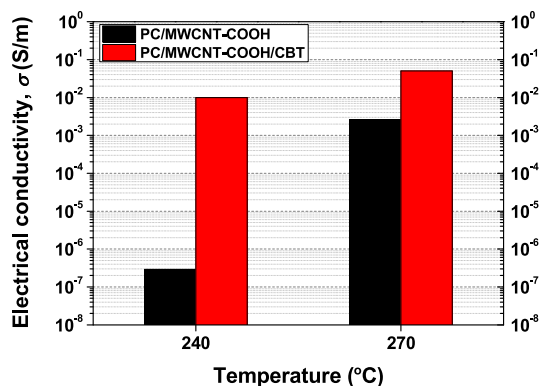


Fig. 6. Electrical conductivity of the composites with 2.5 wt% MWCNT-COOH.

dispersion as compared to non-modified MWCNTs [9]. When processing the composites at 240 °C, the addition of CBT improves the macro-dispersion of MWCNTs, which can be quantitatively proven by the determination of the agglomerate area ratio, A_A . Accordingly, the A_A decreased from $5.2 \pm 1.2\%$ to $4.7 \pm 1.4\%$. With increasing processing temperature, a worse macrodispersion is observed due to lower applied shear stresses in the mixing process. However, an improvement of the MWCNT macrodispersion by adding CBT could be also seen for the composite processed at 270 °C with the A_A being decreased from $6.7 \pm 1.3\%$ to $5.8 \pm 1.2\%$. It is obvious that the PC/CBT blend in the melt state despite lower applied shear stresses can more effectively disperse the MWCNT-COOH compared to the neat PC. This is due to the possible better infiltration of the oligomer from the polymer melt into the MWCNT primary agglomerates being the first step of dispersion [49–51].

Fig. 5 depicts the TEM images of the PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites mixed at 240 and 270 °C. The TEM images provide more detailed information about the percolated MWCNT network within the polymer matrix, which is responsible for the conductive behavior that all the composites exposed. More specific, for the PC/MWCNT-COOH composites mixed at 240 °C, a prominent improvement of the MWCNT dispersion can be seen at the nanoscale level by adding the CBT oligomer. After mixing at 270 °C, the composites show in general a good dispersion of the MWCNT-COOH at the nanoscale level, and no significant differences could be found from the TEM images. Furthermore, with the addition of the cyclic oligomer, the MWCNTs appear longer in the TEM images, which indicates that during the mixing process a less pronounced shortening of the CNTs happened due to the viscosity reduction [51–53].

3.4. Electrical and thermal conductivity of the nanocomposites

Fig. 6 shows that the electrical conductivity values of all the nanocomposites are in the semi-conductive range. The composite prepared at the processing temperature of 240 °C exhibits a conductivity of 2.9×10^{-7} S/m, while after adding the CBT the

conductivity was increased five orders of magnitude to 1.0×10^{-2} S/m. At 270 °C, the nanocomposite shows conductivity of 2.6×10^{-3} S/m, while after adding CBT it was increased to 5.0×10^{-2} S/m. Although the PC/MWCNT-COOH processed at 240 °C show a better filler macrodispersion in the optical microscopy, a lower electrical conductivity was measured. On the other hand, the PC/MWCNT-COOH/CBT processed at 270 °C showed the highest electrical conductivity. This may be due to two factors. Firstly, the effect of secondary agglomeration during mixing and compression molding, shown to enhance the electrical conductivity [54], may be more prominent at 270 °C. In addition it was reported that the percolation threshold and electrical conductivity are strongly determined by the aspect ratio of the filler [55,56]. With a higher processing temperature and the additional use of the cyclic oligomer a less pronounced CNT shortening during the mixing may be assumed and was indicated by the TEM study. This means that these CNTs possess a higher aspect ratio, which finally results in higher electrical conductivity.

The thermal conductivity, κ , was in the range of 0.3 W/m K^{-1} , and slight differences were observed for all the nanocomposites in this study. Table 1 displays the thermal conductivity values of each material, and as it can be observed the MWCNT-COOH have a very small contribution to the thermal conductivity of the neat polycarbonate used as the matrix. The low thermal conductivity that the nanocomposites exhibited is an important characteristic for their utilization as thermoelectric materials. In addition, it should be mentioned that even highly loaded PC/MWCNT composites with 15 wt% MWCNT content showed thermal conductivity values, which remain still lower than 0.6 W/mK^{-1} [57]. The low thermal conductivity facilitates the thermal gradient to be sustained within the materials, which is the main driving force for inducing charge carriers responsible for the obtained thermovoltage.

3.5. Seebeck coefficient (S), power factor (PF) and thermoelectric figure of merit (ZT)

Fig. 7 demonstrates the Seebeck coefficients for the four samples investigated. The Seebeck coefficient was found to be $9.12 \pm 1.74 \mu\text{V/K}$ for the PC/MWCNT-COOH and $12.55 \pm 0.44 \mu\text{V/K}$ for the PC/MWCNT-COOH/CBT nanocomposite processed at 240 °C. An increasing trend after the addition of CBT was found also for the composites prepared at 270 °C. Namely, the Seebeck coefficient was $7.89 \pm 0.8 \mu\text{V/K}$ for the PC/MWCNT-COOH, and $13.55 \pm 0.13 \mu\text{V/K}$ for the PC/MWCNT-COOH/CBT. The CBT additive resulted in an increase

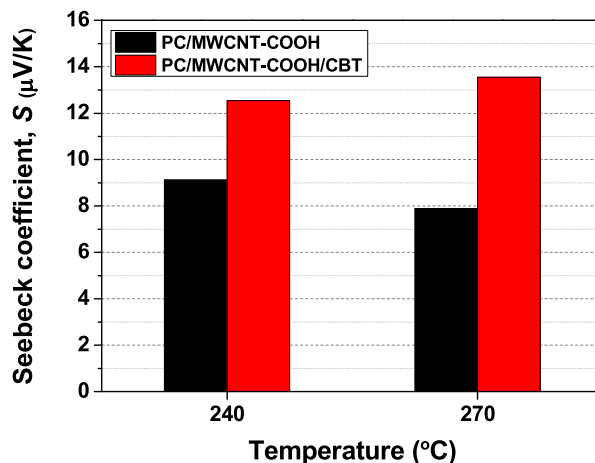


Fig. 7. Seebeck coefficients of PC/MWCNT-COOH and PC/MWCNT-COOH/CBT composites with 2.5 wt% of MWCNT-COOH, prepared at 240 °C and 270 °C.

Table 1
Thermal conductivity for PC and the composites with 2.5 wt% MWCNT-COOH.

Sample	Thermal conductivity, κ (W/m K^{-1})
PC	0.2 ^a
PC/MWCNT-COOH @ 240 °C	0.31
PC/MWCNT-COOH/CBT @ 240 °C	0.27
PC/MWCNT-COOH @ 270 °C	0.29
PC/MWCNT-COOH/CBT @ 270 °C	0.30

^a According to the data sheet of Bayer Material Science.

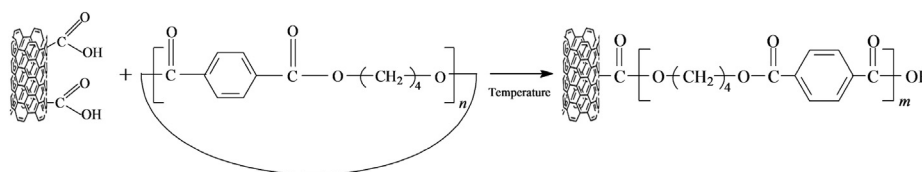


Fig. 8. Possible chemical reaction between MWCNT-COOH and CBT oligomer used as an additive.

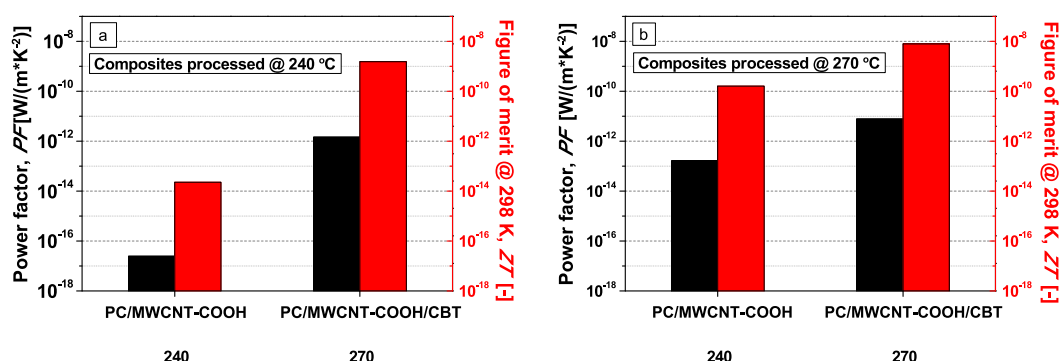


Fig. 9. Power factor (PF) and corresponding thermoelectric figure of merit (ZT) for PC/MWCNT-COOH and PC/MWCNT-COOH/CBT nanocomposites processed at (a) 240 °C, and (b) 270 °C.

of the Seebeck coefficient of 37.6% for the samples processed at 240 °C, and 71.7% for the samples processed at 270 °C. The highest value was found for the PC/MWCNT-COOH/CBT prepared at 270 °C, which can indirectly prove that the $-COOH$ groups of MWCNTs have not been decomposed during the melt-mixing process. Additionally, the CBT additive at both of the processing temperatures was found to increase the Seebeck coefficient values. This could be explained assuming a transesterification reaction between the $-COOH$ groups of MWCNTs with the CBT oligomer, as depicted in Fig. 8. The reaction is envisaged to increase the electronic density of states of MWCNTs due to a p-doping that the CBT facilitates on the MWCNTs.

Fig. 9 represents the power factors (PF) with the corresponding thermoelectric figure of merit values (ZT) for the PC/MWCNT-COOH and PC/MWCNT-COOH/CBT nanocomposites processed at 240 °C (Fig. 9a) and 270 °C (Fig. 9b). The PC/MWCNT-COOH/CBT melt-mixed at 270 °C gives the best compromise to reach the highest value of $ZT = 7.94 \times 10^{-9}$, at room temperature, as well as the highest power factor ($PF = 7.60 \times 10^{-6} \mu W/mK^{-2}$). These values could be attributed to the possible doping of the CBT on the MWCNT-COOH, as well as to the improved electrical conductivity of the PC/MWCNT-COOH/CBT composites due to the fact that the PC/CBT blend imparts enhanced filler dispersion within the polymer matrix. In contrast, the PC/MWCNT-COOH composites show lower PF and ZT , which may be the result of worse filler dispersion observed by optical microscopy, and the absence of CBT, which can act as a dopant.

4. Conclusions

In this study, a cyclic butylene terephthalate (CBT[®] 100) oligomer was applied as a low molecular weight additive in order to allow the processing of polycarbonate (PC) filled with MWCNT-COOH at relatively low temperatures. Since it was the intention to process PC/MWCNT-COOH composites for thermoelectric applications, $-COOH$ functionalised MWCNTs were used in order to get high carrier density due to the carboxyl groups attached onto the MWCNT surface acting as a p-dopant. However, the relatively low thermal stability of the $-COOH$ groups limited the melt-mixing

process to low temperatures to avoid their potential decomposition. To get a matrix processable at lower mixing temperatures, the CBT additive was blended with PC. The CBT addition not only improves the dispersion of MWCNT-COOH within the PC matrix, but the thermoelectric investigations showed that also higher thermoelectric properties were obtained. This could be explained assuming a transesterification reaction of the CBT oligomer with the functional groups on the surface of the nanotubes acting like a molecular dopant of MWCNTs.

It is envisaged that PC/MWCNT-COOH/CBT nanocomposites are ideal candidates for large-scale thermal energy harvesting, considering the ease of processing and the potential for up-scaling the production process. However, in order to enable the commercialization of the proposed materials, the thermoelectric figure of merit has to be increased, which can be achieved by increasing the amount, type, or doping nature and/or level of the conducting fillers. Therefore, preparation of melt-mixed PC composites with higher loadings and the use of differently functionalized/doped MWCNTs could be a promising approach to increase the electrical conductivity as well as the Seebeck coefficient.

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